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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/25427 <b>(22) International Filing Date:</b> 29 October 1999 (29.10.99) <b>(30) Priority Data:</b> 09/181,859 29 October 1998 (29.10.98) US <b>(71) Applicant (for all designated States except US):</b> PHILIP MORRIS INCORPORATED [US/US]; 120 Park Avenue, New York, NY 10017 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KOLLER, Kent, B. [US/US]; 8401 Kintail Drive, Chesterfield, VA 23838 (US). WRENN, Susan, E. [US/US]; 12130 Ivy Mill Road, Chesterfield, VA 23832 (US). HOUCK, Willie, G., Jr. [US/US]; 7753 Lake Forrest Drive, Richmond, VA 23235 (US). PAINE, John, B., III [US/US]; 13630 Trilithon Road, Midlothian, VA 23235 (US). <b>(74) Agent:</b> SKIFF, Peter, K.; Burns, Doane, Swecker & Mathis, L.L.P., P.O. Box 1404, Alexandria, VA 22313-1404 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FILTER FOR SELECTIVE REMOVAL OF A GASEOUS COMPONENT  <b>(57) Abstract</b>  A filter such as an air having a reagent which chemically reacts with and removes a gaseous component of an air stream. The reagent contains functional groups covalently bonded to a non-volatile inorganic substrate which is incorporated in the filter. The filter can remove gaseous components such as aldehydes. Preferred functional groups are 3-aminopropylsilyl groups covalently bonded to silica gel (APS silica gel). The reagent can be contained in a space in the filter or incorporated in one or more filter elements. The reagent can be part of or coated on paper such as filter paper or incorporated in non-paper filter elements formed from fibrous materials such as cellulose acetate or polypropylene fibers. Other preferred reagents include aminoethylaminopropylsilyl silica gel (AEAPS) and aminoethylaminoethylaminopropylsilyl silica gel (AEAEAPS).		

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## FILTER FOR SELECTIVE REMOVAL OF A GASEOUS COMPONENT

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention generally relates to a filter such as air filter. More particularly, the invention relates to a filter that can selectively remove a gaseous component such as aldehydes from a gas mixture, a method of making the filter and a method of removing a gaseous component from a gas mixture.

#### 2. Description of the Related Art

A wide variety of materials have been suggested in the art as filters for tobacco smoke. Such filter materials include cotton, paper, cellulose, and certain synthetic fibers. These filter materials, however, only remove particulates and condensable components from tobacco smoke. They have little or no effect in removing certain gaseous components, e.g., aldehydes, from tobacco smoke.

In light of this, a number of additives have been proposed in the art to supplement the performance of the filter materials. Exemplary additives are mentioned in, for example, U.S. Patent Nos. 2,815,761; 2,881,772; 2,968,306; 3,003,504; and 3,354,886. Some of the additives known in the art are effective in removing certain amounts of gaseous components from tobacco smoke. However, those additives also suffer from various drawbacks.

For example, U.S. Patent No. 2,968,306 discloses the use of certain amino acids, such as glycine, for removing aldehydes in tobacco smoke. It has been discovered that while glycine can reduce the level of formaldehyde in tobacco smoke, it is not stable in the cigarette filter manufacturing process. Moreover, it releases ammonia odor during storage.

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U.S. Patent Nos. 4,604,110 and 4,534,775 disclose an air treatment filter element for removing odors from indoor air. The '110 and '775 patents disclose that the filter element is produced by contacting an adsorbent material such as zeolite, activated carbon and/or silica gel with a liquid for inhibiting growth of microorganisms.

U.S. Patent No. 4,892,719 discloses a furnace filter for removal of indoor pollutants such as formaldehyde or acidic gases such as  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{NO}_x$  and  $\text{H}_2\text{S}$ . The filter includes a polymeric coating with functional groups such as polyallylamine or polyvinylamine for reacting with formaldehyde or acrolein.

U.S. Patent Nos. 4,227,904; 4,374,814; 4,547,350; and 4,724,242 disclose filter arrangements for purifying air. The '904 patent discloses a gas phase permeable filter for home applications such as ductless range hoods, room air purifiers, electronic air cleaners, air conditioners, and heating/ventilating systems and for commercial/industrial applications where fuel exhaust and/or manufacturing operations generate odorants such as sulfur dioxide, formaldehyde, phenols, etc. The odor removing filter can be incorporated in a filter arrangement which also removes smoke, dust, or other particulates. The odor removing material can be flakes, particles, pellets or granules and the filter material can be activated carbon flakes or granules or other substance such as impregnated activated alumina, both of which are adhesively bonded to a porous substrate. A filter is assembled by providing a U-shaped frame around the edges of two such substrates with the bonded particles facing each other. The '350 patent discloses an air filter such as fiberglass or open cell polyurethane which includes a thin layer of polymeric amine such as polyethylenimine, the coating being effective to react with aldehydes and acidic gases. The '242 patent discloses an open-celled foamed gypsum and carbonaceous material for absorbing gases such as carbon monoxide, sulfur dioxide, ozone, ammonia, nitrogen oxides and formaldehyde, the filter material being used as absorbent particles in diapers and undergarments. The '814 patent discloses a filter for removing formaldehyde with a solid shaped

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composition prepared by coating a solid substrate or impregnating a porous or fibrous substrate with a composition including one or more polyhydric water-soluble polymers and water.

While various filter arrangements have been proposed for the removal of pollutants, it is an object of the present invention to provide an improved air filter that can selectively remove aldehydes from ambient air.

Thus, it is an object of the present invention to provide a filter arrangement and, more particularly, an air filter that can selectively remove a gaseous component such as aldehydes from a gas mixture.

#### SUMMARY OF THE INVENTION

The invention provides a filter such as an air filter which incorporates a reagent comprising at least one reactive functional group covalently bonded to a non-volatile inorganic substrate for selective removal of a gaseous component such as an aldehyde from a gas mixture such as ambient air. The reagent is preferably incorporated in a filter element exposed to the gas mixture such that the reactive functional group chemically reacts with aldehyde and removes it from the gas mixture.

It has been surprisingly discovered that a reagent comprising at least one reactive functional group covalently bonded to a non-volatile inorganic substrate is selective in removing a gaseous component such as aldehydes from a gas mixture such as ambient air. According to a preferred embodiment, the reagent can be incorporated in an air filter wherein the reactive functional group chemically reacts with a gaseous component of an air stream to remove it from the air stream.

The preferred functional group is an aminopropylsilyl group such as a 3-aminopropylsilyl group. The preferred substrate is in particle form, and more preferably is silica gel. The most preferred functional group/substrate arrangement (reagent) contains 3-aminopropylsilyl groups bonded to silica gel (hereinafter referred to as "APS silica gel"). This reagent can selectively remove

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gaseous components such as polar compounds (e.g., aldehydes and hydrogen cyanide) from gas mixtures such as ambient air. Other preferred reagents include aminoethylaminopropylsilyl (AEAPS) silica gel and aminoethylaminoethylaminopropylsilyl (AEAEAPS) silica gel.

5                                    BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a perspective partially exploded view of a cigarette constructed in accordance with one embodiment of the present invention wherein folded paper containing a reagent which chemically reacts with a component of cigarette smoke is inserted into a hollow portion of a tubular filter element of the cigarette;

10                                Figure 2 is a perspective partially exploded view of another embodiment of the present invention wherein the reagent is incorporated in folded paper inserted into a hollow portion of a tubular filter element;

                                  Figure 3 is a perspective partially exploded view of another embodiment of the present invention wherein the reagent is incorporated in a plug-space-plug filter  
15                                element;

Figure 4 is a perspective partially exploded view of another embodiment of the present invention wherein the reagent is incorporated in a three-piece filter element having three plugs;

                                  Figure 5 is a perspective partially exploded view of another embodiment of  
20                                the present invention wherein the reagent is incorporated in a four-piece filter element having a plug-space-plug arrangement and a hollow sleeve;

Figure 6 is a perspective partially exploded view of another embodiment of the present invention wherein the reagent is incorporated in a three-part filter element having two plugs and a hollow sleeve;

25                                Figure 7 is a perspective partially exploded view of another embodiment of the present invention wherein the reagent is incorporated in a two-part filter element having two plugs;

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Figure 8 is a perspective partially exploded view of another embodiment of the present invention wherein the reagent is incorporated in a filter element of a cigarette used with an electrical smoking device;

Figure 9 depicts the chemical structures of the starting materials, the intermediate products, and the final APS silica gel reagent of a representative process for preparing the reagent used in the invention;

Figure 10 shows a graphic representation of silica gel wherein the typical Si-O-Si bond angle is  $145^\circ$ , the Si-O bond length is about 1.62 Å and the typical Si-Si distance is about 3.06 Å;

Figure 11 shows a graphic representation of APS silica gel wherein the typical Si-O-Si bond angle is  $145^\circ$ , the Si-O bond length is about 1.62 Å and the typical Si-Si distance is about 3.06 Å;

Figure 12 depicts AEAPS silica gel and its silane precursor;

Figure 13 depicts AEAEAPS silica gel and its silane precursor;

Figure 14 shows a chemical formula representation of how the formaldehyde can be chemically bonded to the APS silica gel when cigarette smoke comes into contact with the APS silica gel;

Figure 15 shows an air filter in accordance with the invention which includes amino-modified silica gel for removing aldehydes from ambient air;

Figure 16 shows a schematic of a process line for incorporating the amino-modified silica gel into fibrous material which can be used for a filter in accordance with the invention; and

Figure 17 is a graph showing results of tests wherein various types of amino-modified silica gel were used to remove formaldehyde from a gas stream.

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#### DETAILED DESCRIPTION OF THE INVENTION

The invention provides a filter arrangement which is effective in removing a component of a gas mixture such as an air stream containing cigarette smoke or ambient air by chemically reacting a reagent with the gaseous component. The



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reagent preferably comprises at least one reactive functional group. In order to prevent the reagent or its reaction product with the targeted gaseous component from being carried back into the gas mixture, the functional group is covalently bonded to an inorganic non-volatile substrate. Such an arrangement is  
5 advantageous over filter arrangements wherein gaseous components are absorbed, adsorbed, or otherwise non-chemically removed from a gas mixture. Such non-chemically removed components may be removed only temporarily and could reenter a gas mixture such as an air stream or if reacted with a volatile reagent, provide products that are themselves volatile and hence could reenter the gas  
10 mixture. According to the present invention, because the reactive functional group is covalently bonded to the substrate, once the gaseous component chemically reacts with the reagent, the removed component (and its reaction products) can be prevented from reentering the gas mixture.

The invention is first explained in connection with a cigarette filter. In the  
15 most preferred embodiment, the reagent is an amino-modified silica gel such as APS silica gel. However, any suitable amino-modified silica gel can be used in accordance with the invention. Without wishing to be bound by theory, it is believed that the APS silica gel contains primary amine groups. Under ordinary smoking conditions, the primary amine groups chemically react with and  
20 covalently bond to the aldehydes in tobacco smoke. The aldehydes are thus selectively removed from the tobacco smoke. Further, since the reactive functional groups and their resulting products from reaction with aldehydes are covalently bonded to the silica gel which is non-volatile, the mainstream tobacco smoke is essentially free of APS silica gel as well as the aldehydes which are  
25 bonded thereto.

Aldehydes in tobacco smoke that can be selectively removed by the reagent of the invention include, but are not limited to formaldehyde, acetaldehyde, acrolein, malonaldehyde, crotonaldehyde, etc.

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In a first preferred embodiment, the reagent such as APS silica gel is incorporated into or onto a support such as paper (e.g., tipping paper) that is located along a filter portion of a cigarette. As will be recognized by persons skilled in the art, such paper can be used, for example, as a wrapper or a liner in the filter portion of the cigarette. The reagent such as APS silica gel can also be loaded onto a support such as lightly or tightly folded paper inserted into a hollow portion of the cigarette filter. The support is preferably in the form of a sheet material such as crepe paper, filter paper, or tipping paper. However, other suitable support materials such as organic or inorganic cigarette compatible materials can also be used.

Figure 1 illustrates a cigarette 2 having a tobacco rod 4, a filter portion 6, and a mouthpiece filter plug 8. As shown, the APS silica gel reagent can be loaded onto folded paper 10 inserted into a hollow cavity such as the interior of a free-flow sleeve 12 forming part of the filter portion 6.

Figure 2 shows a cigarette 2 having a tobacco rod 4 and a filter portion 6, wherein the folded paper 10 is located in the hollow cavity of a first free-flow sleeve 13 located between the mouthpiece filter 8 and a second free-flow sleeve 15. The paper 10 can be used in forms other than as a folded sheet. For instance, the paper 10 can be deployed as one or more individual strips, a wound roll, etc. In whichever form, a desired amount of reagent such as APS silica gel can be provided in the cigarette filter portion by a combination of the coated amount of reagent/area of the paper and/or the total area of coated paper employed in the filter (e.g., higher amounts of APS silica gel can be provided simply by using larger pieces of coated paper). In the cigarettes shown in Figures 1 and 2, the tobacco rod 4 and the filter portion 6 are joined together with tipping paper 14. In both cigarettes, the filter portion 6 may be held together by filter overwrap 11.

The reagent such as APS silica gel can be incorporated into the filter paper in a number of ways. For example, the APS silica gel can be mixed with water to form a slurry. The slurry can then be coated onto pre-formed filter paper and

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allowed to dry. The filter paper can then be incorporated into the filter portion of a cigarette in the manner shown in Figures 1 and 2. Alternatively, the dried paper can be wrapped into a plug shape and inserted into a filter portion of the cigarette. For example, the paper can be wrapped into a plug shape and inserted as a plug  
5 into the interior of a free-flow filter element such as a polypropylene or cellulose acetate sleeve. In another arrangement, the paper can comprise an inner liner of such a free-flow filter element.

Alternatively and more preferably, the reagent such as APS silica gel is added to the filter paper during the paper-making process. For example, the APS  
10 silica gel can be mixed with bulk cellulose to form a cellulose pulp mixture. The mixture can be then formed into filter paper according to methods known in the art.

In another preferred embodiment of the present invention, the reagent such as APS silica gel is incorporated into the fibrous material of the cigarette filter  
15 portion itself. Such filter materials include, but are not limited to, fibrous filter materials including paper, cellulose acetate fibers, and polypropylene fibers. This embodiment is illustrated in Figure 3, which shows a cigarette 2 comprised of a tobacco rod 4 and a filter portion 6 in the form of a plug-space-plug filter having a mouthpiece filter 8, a plug 16, and a space 18. The plug 16 can comprise a tube  
20 or solid piece of material such as polypropylene or cellulose acetate fibers. The tobacco rod 4 and the filter portion 6 are joined together with tipping paper 14. The filter portion 6 may include a filter overwrap 11. The filter overwrap 11 contains traditional fibrous filter material and reagent such as APS silica gel can be incorporated in or on the filter overwrap 11 such as by being coated thereon.

25 Alternatively, the APS silica gel can be incorporated in the mouthpiece filter 8, in the plug 16, and/or in the space 18. Moreover, the APS silica gel can be incorporated in any element of the filter portion of a cigarette. For example, the filter portion may consist only of the mouthpiece filter 8 and the APS silica gel can be incorporated in the mouthpiece filter 8 and/or in the tipping paper 14.

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Figure 4 shows a cigarette 2 comprised of a tobacco rod 4 and filter portion 6. This arrangement is similar to that of Figure 3 except the space 18 is filled with granules of APS silica gel or a plug 15 made of material such as fibrous polypropylene or cellulose acetate containing APS silica gel. As in the previous embodiment, the plug 16 can be hollow or solid and the tobacco rod 4 and filter portion 6 are joined together with tipping paper 14. There is also a filter overwrap 11.

Figure 5 shows a cigarette 2 comprised of a tobacco rod 4 and a filter portion 6 wherein the filter portion 6 includes a mouthpiece filter 8, a filter overwrap 11, tipping paper 14 to join the tobacco rod 4 and filter portion 6, a space 18, a plug 16, and a hollow sleeve 20. The APS silica gel can be incorporated into one or more elements of the filter portion 6. For instance, the APS silica gel can be incorporated into the sleeve 20 or granules of the APS silica gel can be filled into the space within the sleeve 20. If desired, the plug 16 and sleeve 20 can be made of material such as fibrous polypropylene or cellulose acetate containing APS silica gel. As in the previous embodiment, the plug 16 can be hollow or solid.

Figures 6 and 7 show further modifications of the filter portion 6. In Figure 6, cigarette 2 is comprised of a tobacco rod 4 and filter portion 6. The filter portion 6 includes a mouthpiece filter 8, a filter overwrap 11, a plug 22, and a sleeve 20, and the APS silica gel can be incorporated in one or more of these filter elements. In Figure 7, the filter portion 6 includes a mouthpiece filter 8 and a plug 24, and the APS silica gel can be incorporated in one or more of these filter elements. Like the plug 16, the plugs 22 and 24 can be solid or hollow. In the cigarettes shown in Figures 6 and 7, the tobacco rod 4 and filter portion 6 are joined together by tipping paper 14.

Various techniques can be used to apply the reagent such as APS silica gel to filter fibers or other substrate supports. For example, the APS silica gel can be added to the filter fibers before they are formed into a filter cartridge, e.g., a tip

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for a cigarette. The APS silica gel can be added to the filter fibers, for example, in the form of a dry powder or a slurry by methods known in the art. If the APS silica gel is applied in the form of a slurry, the fibers are allowed to dry before they are formed into a filter cartridge.

5 In another preferred embodiment, the reagent such as APS silica gel is employed in a hollow portion of a cigarette filter. For example, some cigarette filters have a plug/space/plug configuration in which the plugs comprise a fibrous filter material and the space is simply a void between the two filter plugs. That void can be filled with the APS silica gel of the present invention. An example of  
10 this embodiment is shown in Figure 3. The APS silica gel can be in granular form or can be loaded onto a suitable support such as a fiber or thread.

In another embodiment of the present invention, the reagent such as APS silica gel is employed in a filter portion of a cigarette for use with a smoking device as described in U.S. Patent No. 5,692,525, the entire content of which is  
15 hereby incorporated by reference. Figure 8 illustrates one type of construction of a cigarette 100 which can be used with an electrical smoking device. As shown, the cigarette 100 includes a tobacco rod 60 and a filter portion 62 joined by tipping paper 64. The filter portion 62 preferably contains a tubular free-flow filter element 102 and a mouthpiece filter plug 104. The free-flow filter element  
20 102 and mouthpiece filter plug 104 may be joined together as a combined plug 110 with plug wrap 112. The tobacco rod 60 can have various forms incorporating one or more of the following items: an overwrap 71, another tubular free-flow filter element 74, a cylindrical tobacco plug 80 preferably wrapped in a plug wrap 84, a tobacco web 66 comprising a base web 68 and tobacco flavor  
25 material 70, and a void space 91. The free-flow filter element 74 provides structural definition and support at the tipped end 72 of the tobacco rod 60. At the free end 78 of the tobacco rod 60, the tobacco web 66 together with overwrap 71 are wrapped about cylindrical tobacco plug 80. Various modifications can be

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made to a filter arrangement for such a cigarette incorporating the reagent of the invention.

In such a cigarette, the reagent such as APS silica gel can be incorporated in various ways such as by being loaded onto paper or other substrate material which is fitted into the passageway of the tubular free-flow filter element 102 therein. It may also be deployed as a liner or a plug in the interior of the tubular free-flow filter element 102. Alternatively, the reagent such as APS silica gel can be incorporated into the fibrous wall portions of the tubular free-flow filter element 102 itself. For instance, the tubular free-flow filter element or sleeve 102 can be made of suitable materials such as polypropylene or cellulose acetate fibers and the reagent such as APS silica gel can be mixed with such fibers prior to or as part of the sleeve forming process.

In another embodiment, the reagent such as APS silica gel can be incorporated into the mouthpiece filter plug 104 instead of in the element 102. However, as in the previously described embodiments, according to the invention, the reagent such as APS silica gel may be incorporated into more than one component of a filter portion such as by being incorporated into the mouthpiece filter plug 104 and into the tubular free-flow filter element 102.

The filter portion 62 of Figure 8 can also be modified to create a void space into which the reagent such as granular APS silica gel can be inserted.

As explained above, the APS silica gel can be incorporated in various support materials. When the APS silica gel is used in filter paper, the silica gel beads or particles may have an average particle diameter of 10 to 100  $\mu\text{m}$ , preferably 40 to 50  $\mu\text{m}$ . When the APS silica gel is used in filter fibers or other mechanical supports, larger silica gel particles may be used. Such particles preferably have a mesh size from 14 to 60, and more preferably from 35 to 60 mesh. The silica gel particles preferably have an average pore size of about 40 to about 250 Å, and more preferably, about 150 Å.

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The amount of APS silica gel employed in the cigarette filter by way of incorporation on a suitable support such as filter paper and/or filter fibers depends on the amount of aldehydes in the tobacco smoke and the amount of aldehydes desired to be removed. As an example, the filter paper and the filter fibers may contain from 10% to 50% by weight of the APS silica gel.

Any commercially available APS silica gel such as that available from J.T. Baker Chemical Co., Philipsburg, New Jersey, can be used in the present invention. It should be noted that the J.T. Baker product is "capped." This means that the free silica gel surface, i.e., the surface that has not been covalently bonded to the APS silica gel groups, is made to be non-polar by coverage with hydrophobic groups.

The APS silica gel can also be made, for example, by mixing aminopropyltriethoxysilane, more preferably 3-aminopropyltriethoxysilane, with silica gel in a water and ethanol solvent. Other solvents, such as toluene, can also be used. The mixture is heated for several hours to allow the 3-aminopropyltriethoxysilane to react with and chemically bond to the silica gel surface. The reaction mixture is then decanted to obtain a reaction product comprising the APS silica gel. The reaction product is subsequently rinsed with a solvent, and dried in an oven at an elevated temperature such as around 100°C or above. Although the rinsing and drying steps are optional, the drying step is preferred. Unlike the J.T. Baker product, the APS silica gel made by this method is not "capped."

The above paragraph describes a process routine which may be practiced with other aminopropyltrialkoxysilanes, such as 3-aminopropyltrimethoxysilane.

The APS silica gel can also be prepared by the following more specific procedure. A suspension of the chosen silica gel is rapidly stirred in a solution of water and ethanol. To that mixture is added a 3-aminopropyltrialkoxysilane compound, preferably 3-aminopropyltriethoxysilane. The 3-aminopropyltrialkoxysilane can be added before, during, or after heating. The

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3-aminopropyltrialkoxysilane is preferably pre-diluted with anhydrous ethanol. The resulting mixture is then heated, preferably to the boiling point. In the most preferred embodiments, the ethanol is distilled off and replaced with water. The solids are isolated by a procedure such as filtration and with an optional solvent  
5 rinse, preferably water. The solids are then heated in an oven until water loss has proceeded to equilibrium with the surroundings. Typical embodiments entail heating overnight at about 105°C.

Figure 9 depicts the most likely mechanism of the reaction that occurs in the making of APS silica gel when 3-aminopropyltriethoxysilane and silica gel are  
10 used as the starting materials. This mechanism is also applicable to other 3-aminopropyltrialkoxysilanes. As shown, when 3-aminopropyltriethoxysilane is contacted with water under appropriate conditions, the ethoxy groups are replaced with hydroxyl so that a 3-aminopropyltrihydroxysilane intermediate is obtained. That intermediate is also believed to undergo a conformational change (which  
15 stabilizes the monomeric form sufficiently to allow it to be used in aqueous medium) before reacting with the silica gel, as shown in Figure 9. Figure 9 further shows the structure of the intermediate reaction product of 3-aminopropyltrihydroxysilane and silica gel. Figure 9 finally shows the cross-linked APS silica gel product after curing. The curing causes the loss of  
20 hydroxyl groups to result in at least a doubly linked silicon anchor for the reactive group.

As shown in Figure 9, each silicon atom of silica gel is tetrahedrally coordinated by four oxygen atoms, which are either singly bonded to two silicon atoms or to a silicon and a proton (OH). The size of the pore (represented in  
25 Figure 9 as a ring) can vary, but is typically about 150Å in diameter.

The 3-aminopropyltriethoxysilane can be obtained commercially from Dow Corning Corp. The silica gel can be obtained commercially from the Grace Davison Division of W.R. Grace & Co.

#### EXPERIMENTAL EXAMPLES



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Preparation of APS Silica Gel Material

Grace Davison 646 (35 X 60 Mesh, 150-angstrom pore size) Silica Gel (circa 1700 to 2000 grams) was placed into a 12-liter Pyrex glass kettle. Distilled water (4 liters) and 95% ethanol (2 liters; 100% ethanol is also acceptable) was added. A clamp-on head had a central neck for the stirring-rod, and three peripheral necks for reagent addition and vapor exit. A stainless steel paddle stirrer was attached to a high-torque (50 inch-pound) digitally controlled stirrer. The high torque stirrer needed to be double-clamped to a sturdy rack system, and served as the point of reference with respect to the kettle. The latter was raised and lowered by a system of "Lab-Jacks," and positioned precisely with respect to the fixed stirrer-rod. The stirrer blade needs to be fairly close to the kettle bottom, but not touching. The blade must never touch the bottom even during "bumping" induced rebound of the flask/kettle. The flask needs to be restrained to prevent motion during "bumping," which is unavoidable, but which the stirring minimizes. A plastic bearing was found to be advantageous since stainless steel bearings were found to be prone to seizing up, and glass bearings were prone to breakage. The mixture was stirred at 200 to 300 RPM, and heated (12 liter mantle, dual heating zone, 100 volts each zone). 3-aminopropyltriethoxysilane (1 x 500 gram bottle), diluted with 100% ethanol (1 liter, including the rinsings) was added as quickly as possible to the stirred heated mixture. (Higher levels of APS functional group incorporation could be achieved by increasing the amount of reagent used).

The ethanol was distilled off. When about 2 liters of aqueous ethanol distillate had collected, water (2 liters) was added to the reaction to restore the original volume. Two more liters of distillate were collected, and two more liters of replacement water were added. The heating was shut off, and stirring was continued until bumping ceased. The mixture was left to cool overnight. The apparatus was dismantled, and the silica was swirled manually and dumped into 4 liter plastic beakers, using recycled supernatant liquid to complete the removal of

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solids. The solids were filtered off onto large (18 to 24 cm diameter) Buchner funnels, with minimal water rinsing (a few hundred milliliters at most). After suction had removed most of the liquid, the moist solids were transferred to stainless steel trays, to dry overnight at 105°C in an oven.

5            Depending on the amount of 3-aminopropyltriethoxysilane employed, relative to the starting silica gel, the dried products showed nominal weight gains ranging from about 8% to about 24%. One of the batches used in the examples below was prepared from 1692.4 grams of Grace Division Silica Gel 646 and 500.1 grams of 3-aminopropyltriethoxysilane under the general conditions described  
10        above. After drying, 1891 grams of APS silica was obtained. A sample was analyzed for C, H, and N. Found: C, 4.21%, H, 1.37%, N, 1.58%. Based on the nitrogen analysis, the 3-aminopropyl content of the silica was 6.55% by weight of product total.

#### Cigarette Testing

15            Several tests were conducted to determine the ability of the cigarette filter of the present invention to remove aldehydes from tobacco smoke as compared to conventional devices. The tests measured the amount of aldehydes removed from the wholestream smoke after the cigarette was fully smoked. WS represents the amount, in %, of aldehydes removed from the wholestream smoke after all the  
20        smoke has been collected and analyzed. TPM represents the amount, in mg/cigarette, of particulate material collected in the filter portion of the cigarette.

             In the following tests, the silica gels used showed a nominal weight gain of about 8 to 25% from the original silica gel during the manufacturing process outlined above. Based on the tests below, a preferred weight gain is around 8 to  
25        16, preferably 10 to 15 wt. %. It is important to note that this weight gain does not refer to weight gain as a result of removing aldehydes. It refers to weight gain from the reaction that adds functional groups such as APS functional groups to the silica gel. APS silica gels that are especially effective when employed in accordance with this invention exhibit a nitrogen content preferably in the range of

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about 1 to 3 percent by weight, and more preferably in the range of about 1.5 to about 2.1 percent.

### Example 1

Filter sections of cigarettes were constructed in accordance with Figure 1 and with the tobacco rod section of Figure 8. A filter section constructed in accordance with the invention identified as Sample 2 contained 16.5 mg of APS silica gel on a folded piece of filter paper 10 (17 mm x 23 mm) inserted in the hollow portion of the tubular filter 12. Another filter section constructed in accordance with the invention identified as Sample 3 contained 21 mg of APS silica gel on a folded piece of filter paper 10 (22 mm x 23 mm) inserted into the hollow portion of the tubular filter 12. A comparative filter section using a folded piece of the filter paper (17 mm x 23 mm) paper (without any APS silica gel) fitted into the hollow portion of the tubular filter was constructed as a control and identified as Sample 1. For Samples 2 and 3, 15 cigarettes were made for TPM measurements and 9 were made for WS measurements. For control Sample 1, 15 cigarettes were made for TPM measurements and 15 for WS measurements. The results are shown in Table 1 below.

Table 1

SAMPLE	TPM	WS
1 Control	2.85	
2 16.5 mg reagent	2.83	~ 61 %
3 21.0 mg reagent	3.11	~ 78 %

### Example 2

Cigarettes similar to those tested in Example 1 included a shorter section containing the APS silica gel. In Samples 1-3, the filter section was constructed in accordance with Figure 2 and included a 16 mm sleeve 13, a 7 mm sleeve 12,

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and a 7 mm filter plug 8. The sleeve 12 contained a folded sheet (7 mm x 75 mm) of APS silica gel coated or uncoated paper. Three samples identified as control Sample 1 (uncoated paper), Sample 2 (paper coated with 11 mg APS silica gel), and Sample 3 (paper coated with 22 mg APS silica gel) were tested. 15 cigarettes of each sample were made for TPM measurement and 9 for WS measurement. The results are shown in Table 2 below.

Table 2

SAMPLE	TPM	WS
1 (Control)	3.37	
2 11 mg reagent	3.14	~ 69%
3 22 mg reagent	2.35	~ 78%

Example 3

Cigarettes were constructed in accordance with a more conventional cigarette having a tobacco rod like that shown in Figure 2 and a conventional filter element. Sample 1 is a control sample without APS silica gel and Sample 2 contained 50 mg APS silica gel in the filter element. The WS was measured for each and the results are shown in Table 3.

Table 3

Sample	WS
1 Control	
2 50 mg reagent	~71%

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Example 4

Cigarettes were constructed in accordance with Figure 8 having APS silica gel contained in the mouthpiece filter. Sample 1 is a control sample which did not include APS silica gel and Samples 2 and 3 contained APS silica gel in the mouthpiece filter 104 which was 7 mm long. The samples also included a sleeve 102 adjacent the mouthpiece filter which was 23 mm long and constructed of polypropylene. In Sample 3, 11 mg APS silica gel was included in an additional polypropylene sleeve 74 having a length of 7 mm and located in the tobacco rod at an end thereof adjacent the filter element. The WS was measured for each and the results are shown in Table 4.

Table 4

	SAMPLE	WS
1	Control	
2	Polypropylene mouthpiece filter with 12 mg reagent	~46%
3	Polypropylene mouthpiece filter with 11 mg reagent	~41%

15

Example 5

Cigarettes were constructed in accordance with Figure 8 having APS silica gel contained in various filter elements. The cigarettes were tested for WS and TPM levels and the results are shown in Table 5 below.

Table 5

	SAMPLE	TPM	WS
1	Control		
2	Polypropylene sleeve 102 with 40 mg reagent and second polypropylene sleeve 74 with 11 mg reagent	5.88	~38%
3	Polypropylene sleeve 102 with 40 mg reagent	5.11	~35%

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4	Cellulose acetate sleeve 102 with 50 mg reagent	4.71	~35%
5	Polypropylene sleeve 102 with 25 mg reagent and 25 mg carbon	5.73	~33%

All samples had a 23 mm long sleeve 102 in the filter portion and a 7 mm long mouthpiece filter 104. In Sample 2, the second sleeve 74 containing the APS silica gel was located in the tobacco rod adjacent the filter portion and had an inner diameter of 4.0 mm. In Samples 3-5, a second sleeve 74 similar to that of Sample 2 but without the APS silica gel had an inner diameter of 3.5 mm.

#### Example 6

Cigarettes were constructed in accordance with the plug-space-plug embodiment shown in Figure 5. In each cigarette, the tubular free-flow filter element 20 was 13 mm long, the filter plug 8 was 5 mm long, the filter plug 16 was 7 mm long, and the void space 18 was 5 mm long. Control Samples 1 and 3 contained 50 mg of silica gel without any APS silica gel in the void space 18 and Samples 2 and 4 included APS silica gel particles weighing 50 mg in the void space 18. WS was measured and the results are shown in Table 6 below.

Table 6

SAMPLE	WS
1 (Control)	~50%
2	~87%
3 (Control)	~78%
4	over 93%

#### Example 7

The cigarettes used for Samples 2 and 3 in Table 7 below were constructed in accordance with the embodiments shown in Figures 6 and 7, respectively. In Sample 2, the tubular filter element 20 was 16 mm long, the filter plug 8 was 7

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mm long, and the solid plug 22 was 7 mm long and comprised of a hand rolled mixture of APS silica gel and polypropylene fibers. In Sample 3, the plug 24 was 23 mm long and comprised of a hand rolled mixture of APS silica gel and polypropylene fibers and the filter plug 8 was 7 mm long. Sample 1 was a control cigarette. Measurements were made of TPM and WS. The results are shown in Table 7 below.

Table 7

SAMPLE	TPM	WS
1		
2	3.92	~ 66%
3	Not tested	~ 81%

According to the invention, the surface of silica gel can be chemically modified to achieve desired selective filtration properties. In the case of APS silica gel, the aminopropylsilyl group is attached to the silica gel skeleton by one or more covalent silicon-oxygen-silicon bonds. The primary amine group at the terminal (exposed or free) end of the aminopropylsilyl group readily reacts with aldehydes and ketones. The primary amine reacts with the aldehyde to form an imine and/or other covalently bonded derivatives of the aldehyde. The imine group or other covalently bonded derivative of the aldehyde remains anchored to the silica gel and thus the formation of such derivatives serves to effectively remove the aldehydes and ketones and their reaction products from cigarette smoke. The primary amine group also reacts with hydrogen cyanide through an acid-base reaction thus reducing the levels of this compound in the cigarette smoke.

Silica gel is a variably hydrous form of silicon dioxide sometimes called "silicic acid" which can be prepared by precipitation by an acid from a solution of sodium silicate. The silica gel can be characterized as a porous disordered three-dimensional polymer of siloxane tetrahedra, forming sheets, ribbons, chains and

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frameworks with various pore-sizes permeating the whole, formed by the variable nature of the cross-linking of the overall three-dimensional structure. Each silicon atom is bonded to four oxygen atoms, at the corners of a tetrahedron. The oxygen atoms are mostly bonded to two silicon atoms but some can be bonded to a single silicon atom and one hydrogen atom to generate a "silanol" functionality. The majority of oxygen atoms are "siloxane" oxygen atoms which are bonded to two silicon atoms. Some silicon atoms called "germinal" silanediols are bonded to two silanol oxygens. The vast majority of silanol groups consist of a silicon atom with one hydroxyl group and three siloxane oxygens. Such silanols may be isolated from one another but when adjacent each other are referred to as "vicinal" silanols (oxo-bis-silanols). Any such silanol functionality provides a point of attachment for derivatizing groups such as 3-aminopropylsilyl. Figure 10 shows a graphic representation of silica gel wherein the typical Si-O-Si bond angle is  $145^\circ$ , the Si-O bond length is about  $1.62 \text{ \AA}$  and the typical Si-Si distance is about  $3.06 \text{ \AA}$ .

APS silica gel can be characterized as silica gel which has been modified at some of the hydroxyl groups by the derivatizing reagent 3-aminopropyltriethoxysilane which permanently attaches 3-aminopropylsilyl (APS) groups to the porous silica gel framework. The attached 3-aminopropylsilyl groups can react with targeted carbonyl group containing substrates. Figure 11 shows a graphic representation of APS silica gel wherein the typical Si-O-Si bond angle is  $145^\circ$ , the Si-O bond length is about  $1.62 \text{ \AA}$  and the typical Si-Si distance is about  $3.06 \text{ \AA}$ . The 3-aminopropylsilyl groups can be considered basic in that they can remove acids such as hydrogen cyanide from mainstream cigarette smoke. In preparing such APS silica gel it is preferred that the silica gel have a large average pore diameter. For instance, whereas "desiccant" silica gel has a pore size on the order of  $20 \text{ \AA}$ , a preferred pore size for the APS silica gel is on the order of  $60$  to  $150 \text{ \AA}$ . Large pore-sized silica gel can be obtained from the



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Davison Chemical Division of the W.R. Grace & Company, Baltimore, Maryland.

One technique for making such large pore-sized silica gel is by mixing a sodium silicate solution with dilute sulfuric acid, allowing the solution to gel over time, washing with water (for several days), drying and grinding the silica gel. In converting the silica gel into APS silica gel, the silica gel of the desired particle size can be heated with the derivatizing reagent 3-aminopropyltriethoxysilane in a solvent such as water, ethanol, toluene or the like, and heat-drying the reaction product to "cure" the product. Any unused reagent can be recycled during production of other batches of APS silica gel.

The APS silica gel can be prepared using other derivatizing reagents. For instance, another derivatizing reagent which can be used is 3-aminopropyltrimethoxysilane which generates methanol during the manufacturing process. In contrast, 3-aminopropyltriethoxysilane generates ethanol. In addition, the silica gel can be modified to incorporate groups in addition to or instead of the APS. For example, the silica gel can be modified to form aminoethylaminopropylsilyl (AEAPS) silica gel which can be made using N-[3-(trimethoxysilyl)propyl]-ethylenediamine (Chemical Abstracts Service Registry No. 1760-24-3) as the derivatizing reagent. Figure 12 depicts the chemical structures of the starting silane and the final AEAPS silica gel. Alternatively, the silica gel can be modified to form aminoethylaminoethylaminopropylsilyl (AEAEAPS) silica gel which can be made using N<sup>1</sup>-[3-(trimethoxysilyl)propyl]-diethylenetriamine (Chemical Abstracts Service Registry No. 35141-30-1) as the derivatizing reagent. Figure 13 depicts the chemical structures of the starting silane and the final AEAEAPS silica gel. The above described APS, AEAPS and AEAEAPS surface modified silica gels can be made in commercial quantities by economic manufacturing conditions. It is contemplated that any covalently bonded amine group attached to silica such as homologues or analogues with

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additional amine functionality can also be used as a component of an air filter such as a cigarette filter in accordance with the invention.

During filtration, the APS silica gel can permanently remove select gaseous components from an airstream such as mainstream tobacco smoke. For instance, by incorporating the APS silica gel in a cigarette filter, cigarette paper, tobacco filler and/or tobacco containing sheet material of a cigarette, the APS silica gel can be used to selectively remove formaldehyde from tobacco smoke. Figure 14 shows a chemical formula representation of how the formaldehyde can be chemically bonded to the APS silica gel when cigarette smoke comes into contact with the APS silica gel.

While the invention has been described so far with reference to a cigarette filter, the invention also provides a filter which is effective in removing a component of a gas mixture such as ambient air by chemically reacting a reagent therewith. As in the case of the cigarette filter described above, the reagent of the air filter preferably comprises at least one reactive functional group. Once the targeted ambient air component chemically reacts with the reagent, the reagent or its reaction product cannot pass into the gas mixture since the functional group is covalently bonded to an inorganic non-volatile substrate.

According to a preferred embodiment, the reagent is incorporated in a gas phase permeable filter for home applications such as ductless range hoods, room air purifiers, electronic air cleaners, air conditioners, and heating/ventilating systems. The filter can also be used in commercial/industrial applications where fuel exhaust and/or manufacturing operations generate odorants such as sulfur dioxide, formaldehyde, phenols, etc. The filter according to the invention can be incorporated in a filter arrangement which also removes smoke, dust, or other particulates. The filter can include odor removing material in the form of flakes, particles, pellets or granules. The filter can include known filter materials such as activated carbon flakes or granules or other substances such as impregnated activated alumina. The gas phase permeable portion of the filter can be made of

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various materials such as fiberglass or open cell polyurethane. The reagent according to the invention can be incorporated in such filters by a variety of techniques, some of which are described above in connection with the cigarette filter and additional techniques are described below. In a preferred embodiment, 5 the reagent comprises the amino-modified silica gel such as APS, AEAPS or AEAEAPS discussed above in connection with the cigarette filter.

According to one embodiment of the invention, the amino-modified silica gel is coated onto a substrate forming part of an air filter. For example, the amino-modified silica gel can be coated on an air permeable portion of the air 10 filter. Alternatively, the amino-modified silica gel can be coated on or entrained in a fibrous material such as cotton, glass wool, rock wool, chopped polyolefin, nylon, polyester, rayon and other fibers, etc. The fibrous material can be in the form of a filament, yarn, ribbon, sheet, etc. of organic or synthetic material. A preferred method of coating a strand of fibrous material is by passing the strand 15 through an adhesive and then through a bed of the amino-modified silica gel particles to attach the amino-modified silica gel particles to the strand. The strand can be incorporated in a filter element by various techniques which will be apparent to those skilled in the art, e.g., the strand can be chopped into pieces which are mixed with other materials to form a filter element or the strand can be 20 formed into a woven or non-woven fabric which is incorporated into a filter element. However, a filter element can be dipped or sprayed with a solution of the APS silica gel, e.g., a solution of the amino-modified silica gel can be sprayed or spread onto a nonwoven material such as paper, polyolefin, polyester, nylon, rayon, glass fiber web, a woven cloth or fabric or screening material including 25 drapery or netting of organic or inorganic materials. Any technique by which the amino-modified silica gel can be incorporated into an air filter is considered within the scope of the invention.

The amino-modified silica gel can also be used as loose particles contained in an air permeable enclosure such as a permeable bag or perforated container

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which can be suspended in open air, hung on a wall, supported on a shelf or placed in an airstream traveling to or from an air conditioning or heating system. However, the amino-modified silica gel particles can also be bonded to one or both sides of an air permeable substrate which can be used alone or in a stack of such substrates as part of an air filter. Another possibility is to bond the amino-modified silica gel particles to each other to form a three dimensional air filter element which is self supporting or supported by another part of an air filter.

According to a preferred embodiment, the amino-modified silica gel is incorporated in a replaceable air filter element. For example, such an air filter can be part of a portable air filtration system or a replaceable filter cartridge or panel of a heating/air conditioning unit. It is contemplated that the air filter could be used in homes, offices, hospitals, schools, governmental or commercial buildings, universities, manufacturing facilities, and the like. The filter will be especially useful in treating the air in newly constructed or remodeled facilities wherein formaldehyde is an obnoxious pollutant produced by gaseous release from resin used in particle board or plywood or by urea-formaldehyde foam insulation used in building or furniture construction. That is, the urea-formaldehyde resin commonly used in plywood/particle board and foam insulation can release gaseous formaldehyde into the ambient air in sufficient quantities to cause irritation or even serious medical problems for certain people exposed to the pollutant. The amino-modified silica gel according to the invention is highly advantageous in reducing or eliminating formaldehyde in the ambient air.

According to one embodiment of the invention, amino-modified silica gel consists of large pore-size silica gel, which has been modified by the covalent chemical attachment of 3-aminopropylsilyl groups thereto (i.e., APS silica gel). The APS silica gel is effective for irreversibly binding ambient aldehydes, permanently anchoring them (after chemical reaction) to the silica gel in non-volatile form. Thus, for the purpose of unencumbered reaction with gaseous components, the amine-group of the 3-aminopropyl substituent is left "free"

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instead of being further modified by derivatizing reagents. A packed bed of moderately coarse granular APS silica gel, of sufficient depth to provide adequate contact-time with minimal pressure-drop, can be used to effectively filter aldehydes from large volumes of ambient air in an efficient manner.

5 In a first preferred embodiment, the reagent such as APS silica gel is incorporated in an air filter such as a 16 inch x 20 inch x 1 inch fiberglass air filter. The air filter can be made of gas phase permeable substrate materials other than fiberglass and the air filter can include ingredients for selectively removing airstream components other than aldehydes. For example, the reagent such as  
10 APS silica gel can be loaded onto supports such as activated carbon or charcoal, alumina, woven or non-woven fabric, polyurethane foam, polymeric, ceramic, metallic, and organic materials such as cellulose acetate. The support is preferably in the form of a sheet or mat of material or composite of loose or bonded particles. Figure 15 illustrates a filter 30 having an air permeable filter  
15 element 32 containing APS silica gel and a frame 34 surrounding the filter element.

Figure 16 shows a processing line 40 wherein a strand 42 of fibrous material is passed through a bath 44 of adhesive and then through a bed 46 of APS silica gel particles whereby APS silica gel particles are adhered to the strand 42.  
20 As indicated earlier, the strand can be chopped into pieces and used alone or mixed with other materials as part of a filter element, e.g., the chopped fibers can be mixed with fiberglass and the fiber mixture can be formed into a filter element such as the filter element 32 shown in Figure 15.

Another technique for forming filter elements having amino-modified silica  
25 gel incorporated therein is by papermaking techniques wherein the amino-modified silica gel particles are mixed with the pulp used to form the paper or the amino-modified silica gel can be applied as a coating to the paper after it is formed. The paper coating technique offers advantages in achieving a desired amount of the amino-modified silica gel in a filter element, e.g., by controlling the coated

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amount of reagent/area of the paper and/or the total area of coated paper employed in the filter (e.g., higher amounts of amino-modified silica gel can be provided simply by using larger pieces of coated paper or heavier coatings on the paper).

5           The reagent such as amino-modified silica gel can be incorporated into filter paper in a number of ways. For example, the amino-modified silica gel can be mixed with water to form a slurry. The slurry can then be coated onto pre-formed filter paper and allowed to dry. The filter paper can then be incorporated into an air filter as a single layer or as part of a multi-layer composite wherein the  
10 filter paper is an outer or inner layer of the composite. Alternatively, the dried paper can be molded into a three dimensional shape or wrapped into an air permeable cylindrical shape. In another arrangement, the paper can comprise a liner of air filter. If the amino-modified silica gel is added to the ingredients of filter paper during the paper-making process, the amino-modified silica gel can be  
15 mixed with bulk cellulose to form a cellulose pulp mixture and the mixture can then be formed into filter paper according to methods known in the art.

Various techniques can be used to apply the reagent such as amino-modified silica gel to filter fibers or other substrate supports. For example, the amino-modified silica gel can be added to the filter fibers before they are formed into a filter element, e.g., the amino-modified silica gel can be added to the filter  
20 fibers, for example, in the form of a dry powder or a slurry by methods known in the art. If the amino-modified silica gel is applied in the form of a slurry, the fibers may be dried before they are formed into a filter element.

In another preferred embodiment, the reagent such as amino-modified  
25 silica gel is employed as a mass of particles in an air permeable enclosure. However, the particles of the amino-modified silica gel can be mixed with other materials such as substances which filter other components from the air. The amino-modified silica gel can be in granular form or loaded onto a support

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material such as a paper, organic or inorganic particulate material, fibers, thread, etc.

As explained above, the amino-modified silica gel can be incorporated in various support materials. When the amino-modified silica gel is used in filter paper, the silica gel beads or particles may have an average particle diameter of 10 to 100  $\mu\text{m}$ , preferably 40 to 50  $\mu\text{m}$ . When the amino-modified silica gel is used in filter fibers or other mechanical supports, larger silica gel particles may be used. Such particles preferably have a mesh size from 14 to 60, and more preferably from 35 to 60 mesh. The silica gel particles preferably have an average pore size of about 40 to about 250  $\text{\AA}$ , and more preferably, about 150  $\text{\AA}$ . An advantage of the APS silica gel reagent according to the invention is that formaldehyde can be selectively and permanently removed from the ambient air. In contrast, formaldehyde removed from an airstream by filter materials such as unmodified silica gel (i.e., silica gel without the APS) absorb rather than chemically react with the formaldehyde. As a result, formaldehyde absorbed by such unmodified silica gel could release the formaldehyde back into the airstream.

Figure 17 shows results of tests carried out to determine the formaldehyde absorbing ability of various amino-modified silica gels. In the results shown in Figure 17, curve A represents mercaptopropylsilane MPS corresponding to the formula:  $\equiv\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-SH}$ , curve B represents AEAEAPS corresponding to the formula:  $\equiv\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$ , curve C represents AEAPS corresponding to the formula:  $\equiv\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$ , curve D represents 35x60 mesh APS corresponding to the formula:  $\equiv\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$ , curve E represents 14x40 mesh APS and curve F represents an additional APS sample. During the tests, 30 mg of amino-modified silica gel was loaded in a non-packed condition in a plug-space-plug configuration wherein a cellulose acetate filter was used as a holder for the sample. The length of the filter bed can be calculated based on the packing density of the amino-modified silica gel sample and diameter of the holder. Using 22 pounds/cubic

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foot ( $5775 \text{ mg/in}^3$ ) as the density of the silica gel, the volume of the 30 mg sample is calculated as  $0.0052 \text{ in}^3$ , the measured flow rate of the gas stream (a predetermined amount of formaldehyde in nitrogen) was  $160 \text{ cm}^3/\text{min}$ , and the contact time was calculated as 32 ms. Curves A and B are estimated to terminate at about 0.016 Absorbance Units (AU) corresponding to formaldehyde concentrations of about 48 ppm, curves C and D are estimated to terminate at about 0.014 AU corresponding to formaldehyde concentrations of about 42 ppm, and curve E is estimated to terminate at about 0.013 AU corresponding to formaldehyde concentrations of about 39 ppm. According to the U.S. Environmental Protection Agency, formaldehyde levels as low as 0.1 ppm can cause "watery eyes, burning sensations in the eyes and throat, nausea, and difficulty breathing in some humans." Although the results shown in Figure 17 were not conducted at such low formaldehyde levels, the results demonstrate that an air filter containing the amino-modified silica gel according to the invention should be capable of removing low levels of formaldehyde from ambient air. For example, in adapting the air filter according to the invention for air purification of a standard room size, an air flow rate of  $30 \text{ ft}^3/\text{min}$  could be used to filter air through a 15 inch by 9.5 inch air filter in accordance with the invention.

From the foregoing test results it is estimated that 1 mol of the AEAPS traps 2 mols of formaldehyde gas. With respect to the shapes of the curves in Figure 17, the longer the curve stays low (i.e., the curve is closer to 0 AU), the higher the capacity of the filtration agent. Based on the test results, it appears that AEAPS and AEAEAPS exhibit the best behavior in this regard.

The experiments indicate that the amino-modified silica gel is effective in removing formaldehyde from a gas stream wherein nitrogen is the carrier gas. Such results suggest that the amino-modified silica gel will also remove aldehydes from ambient air, especially in view of the results discussed above with respect to removal of aldehydes from cigarette smoke which is an air stream containing tobacco smoke. Further, the filter according to the invention can be used to



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remove select gaseous components from non-air streams such as waste gas streams in industrial processes. Accordingly, the filter according to the present invention can be used for a wide assortment of filtering applications.

While the invention has been described with reference to preferred  
5 embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the invention as defined by the claims appended hereto. For example, the ring structure  
10 depicted in Figure 9 is representative of a wide range of ring sizes present within the highly disordered silica gel structure, and is not intended to exclude other sizes of ring from consideration as components of the matter covered by this patent application.

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Claims:

1. A filter comprising a reagent consisting essentially of at least one reactive functional group covalently bonded to a non-volatile inorganic substrate wherein the reagent chemically reacts with a gaseous component of a gas stream to remove the gaseous component from the gas stream.  
5
2. The filter according to claim 1, wherein the reagent comprises a coating on a filter element or a coating on a strand of fibrous material forming a filter element or particles such as silica gel or a shaped article.
3. The filter according to claim 1, wherein the functional group is an aminopropylsilyl group such as a 3-aminopropylsilyl group or a N-[2-aminoethyl]-  
10 3-aminopropylsilyl group or a N-[3-aminoethyl]-3-aminopropylsilyl group or a N-[N-(2-aminoethyl)-2-aminoethyl]-3-aminopropylsilyl group.
4. The filter according to claim 1, wherein the substrate comprises filter fibers and the reagent is covalently bonded to the filter fibers preferably in an  
15 amount of 10 to 50% by weight.
5. The filter according to claim 1, wherein the gaseous component to be removed is polar such as an aldehyde.
6. The filter according to claim 1, wherein the reagent is incorporated in filter paper optionally arranged as adjacent layers in the filter or folded into a three-  
20 dimensional shape or arranged as a single layer in the filter.
7. The filter according to claim 1, wherein the reagent is incorporated with cellulose acetate fibers and/or polypropylene fibers.

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8. The filter according to claim 1, wherein the reagent is incorporated in a cavity of the filter or the reagent is incorporated in a carpet or drapery material.
9. The filter according to claim 1, wherein the filter comprises a replaceable filter element of an air ventilation system.
- 5 10. A filter which comprises an amino-modified silica gel wherein the functional group is an aminopropylsilyl group or an aminopropylsilyl group further substituted on nitrogen by one or more aminoalkyl or poly(aminoalkyl) functional groups.
- 10 11. The filter according to claim 10, wherein the filter is incorporated in an air ventilation system.
12. The filter according to claim 11, wherein amino-modified silica gel comprises an aminopropylsilyl group covalently bonded to the silica gel.
- 15 13. The filter according to claim 12, wherein the functional group includes a 3-aminopropylsilyl group or a N-[2-aminoethyl]-3-aminopropylsilyl group or a N-[3-aminoethyl]-3-aminopropylsilyl group or a N-[N-(2-aminoethyl)-2-aminoethyl]-3-aminopropylsilyl group.
14. The filter according to claim 10, wherein the amino-modified silica gel comprises a coating on a filter element or a coating on a strand of fibrous material forming a filter element or particles such as silica gel or a shaped article.
- 20 15. The filter according to claim 10, wherein the amino-modified silica gel is incorporated in filter paper optionally arranged as adjacent layers in the filter or folded into a three-dimensional shape or arranged as a single layer in the filter.

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16. The filter according to claim 10, wherein the amino-modified silica gel is incorporated with cellulose acetate fibers and/or polypropylene fibers.
17. The filter according to claim 10, wherein the amino-modified silica gel is incorporated in a cavity of the filter or the reagent is incorporated in a carpet or  
5 drapery material.
18. The filter according to claim 10, wherein the filter comprises a replaceable filter element of an air ventilation system.
19. The filter according to claim 10, wherein the amino-modified silica gel has an average particle diameter of at least 10  $\mu\text{m}$  or the amino-modified silica gel is  
10 in the form of particles having a mesh size of at least 60.
20. The filter according to claim 10, wherein the total nitrogen content of the amino-modified silica gel is in the range of approximately 1 to 3 percent by weight, preferably 1.5 to 2.1 percent by weight.
21. A method of manufacturing a filter which is useful for removing a gaseous  
15 component of a gas mixture, comprising steps of:  
    preparing a reagent comprising at least one reactive functional group covalently bonded to a non-volatile inorganic substrate; and  
    incorporating the reagent in a filter wherein the reagent chemically reacts with a gaseous component of a gas mixture to remove the gaseous component  
20 from the gas mixture.
22. The method according to claim 21, wherein the reagent is effective in removing a polar gaseous component such as an aldehyde from the gas mixture.

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23. The method according to claim 21, wherein the reagent is prepared such that the functional group includes a 3-aminopropylsilyl group or a N-[2-aminoethyl]-3-aminopropylsilyl group or a N-[3-aminoethyl]-3-aminopropylsilyl group or a N-[N-(2-aminoethyl)-2-aminoethyl]-3-aminopropylsilyl group.
- 5 24. The method according to claim 23, wherein the reagent is prepared by reacting silica gel with an aqueous or non-aqueous solution containing 3-aminopropyltriethoxysilane or 3-aminopropyltrimethoxysilane or N-[3-(trimethoxysilyl)propyl]-ethylenediamine or N<sup>1</sup>-[3-(trimethoxysilyl)propyl]-diethylenetriamine.
- 10 25. The method according to claim 21, wherein the functional group is an aminopropylsilyl group such as a 3-aminopropylsilyl group.
26. The method according to claim 21, wherein the reagent is incorporated in the filter by coating the reagent on a filter element or coating the reagent on a strand of fibrous material forming a filter element.
- 15 27. The method according to claim 21, wherein the substrate comprises filter fibers and the reagent is covalently bonded to the filter fibers preferably in an amount of 10 to 50% by weight.
28. The method according to claim 21, wherein the reagent is incorporated in filter paper optionally arranged as adjacent layers in the filter or folded into a  
20 three-dimensional shape or arranged as a single layer in the filter.
29. The method according to claim 21, wherein the reagent is incorporated with cellulose acetate fibers and/or polypropylene fibers.

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30. The method according to claim 21, wherein the reagent is incorporated in a cavity of the filter or the reagent is incorporated in a carpet or drapery material.
31. The method according to claim 21, wherein the filter comprises a replaceable filter element of an air ventilation system.
- 5 32. The method according to claim 21, wherein the reagent comprises amino-modified silica gel having an average particle diameter of at least 10  $\mu\text{m}$  or the reagent comprises amino-modified silica gel in the form of particles having a mesh size of at least 60.
- 10 33. The method according to claim 32, wherein the total nitrogen content of the amino-modified silica gel is in the range of approximately 1 to 3 percent by weight, preferably 1.5 to 2.1 percent by weight.
- 15 34. A method of removing a gaseous component of a gas mixture, comprising passing the gas mixture in contact with a filter comprising a reagent comprising at least one reactive functional group covalently bonded to a non-volatile inorganic substrate such that the reagent chemically reacts with the gaseous component of the gas mixture and removes the gaseous component from the gas mixture.
- 20 35. The method according to claim 34, further comprising steps of generating the gas mixture and directing a gas stream containing the gas mixture into contact with the filter such that the component of the gas mixture to be removed is chemically reacted with the reagent and prevented from reentering the gas stream.
36. The method according to claim 34, wherein the functional group is an aminopropylsilyl group effective to remove an aldehyde component from the gas

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mixture, the gas mixture being passed into contact with the reagent such that the aldehyde component is removed from the gas mixture.

37. The method according to claim 34, wherein the functional group is a 3-aminopropylsilyl group effective to remove formaldehyde from the gas mixture, the gas mixture being passed into contact with the reagent such that the formaldehyde is removed from the gas mixture.
38. The method according to claim 34, wherein the reagent comprises amino-modified silica gel located in one or more filter elements, the gas mixture being passed into contact with the one or more filter elements.
39. The method according to claim 34, wherein the substrate comprises particles or a shaped article, the gas mixture being passed into contact with a mass of the particles or into contact with the shaped article.
40. The method according to claim 34, wherein the reagent is incorporated in filter paper optionally formed into a three-dimensional shape or the reagent is combined with fibers which are formed into a filter element, the gas mixture being passed into contact with the filter paper or the filter element.
41. The method according to claim 34, wherein the reagent is combined with an air permeable filter body, the gas mixture being passed into contact with the filter body such that the reagent chemically reacts with the gaseous component and removes the gaseous component from the gas mixture.
42. The method according to claim 34, wherein the substrate comprises filter fibers such as polypropylene and/or cellulose acetate fibers and the reagent is covalently bonded to the filter fibers in an amount of 10 to 50% by weight, the

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gas mixture being passed into contact with the filter fibers such that the gaseous component reacts with the reagent and the gaseous component is removed from the gas mixture.

43. The method according to claim 34, wherein the functional group includes a  
5 3-aminopropylsilyl group or a N-[2-aminoethyl]-3-aminopropylsilyl group or a N-[3-aminoethyl]-3-aminopropylsilyl group or a N-[N-(2-aminoethyl)-2-aminoethyl]-3-aminopropylsilyl group, the gas mixture being passed into contact with the reagent.
44. The method according to claim 34, wherein the reagent comprises amino-  
10 modified silica gel having a total nitrogen content in the range of approximately 1 to 3 percent by weight, preferably 1.5 to 2.1 percent by weight, the gas mixture being passed into contact with the reagent.
45. The method according to claim 34, wherein the reagent is incorporated in a  
15 cavity of the filter or the reagent is incorporated in a carpet or drapery material, the gas mixture being passed into contact with the reagent.
46. The method according to claim 34, wherein the filter comprises a replaceable filter element of an air ventilation system, the gas mixture comprising ambient air passed into contact with the filter element.
- 20 47. The method according to claim 34, wherein the reagent comprises amino-modified silica gel having an average particle diameter of at least 10  $\mu\text{m}$  or amino-modified silica gel in the form of particles having a mesh size of at least 60, the gas mixture being passed into contact with the reagent.



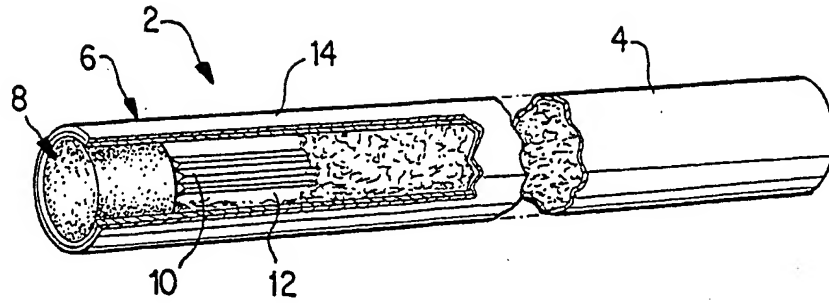


FIG. 1

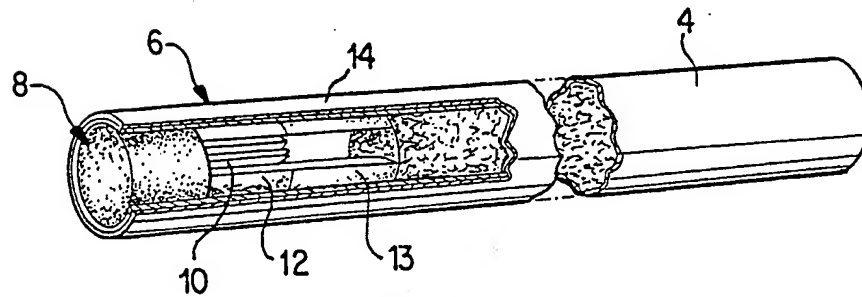


FIG. 2

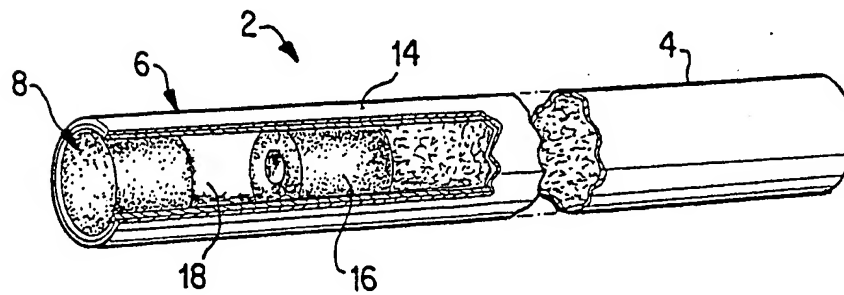


FIG. 3

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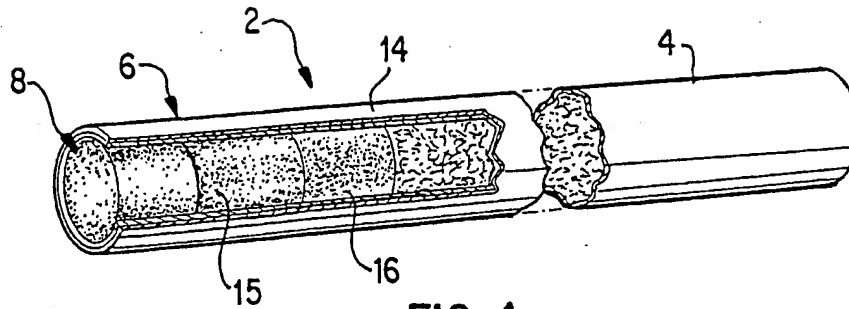


FIG. 4

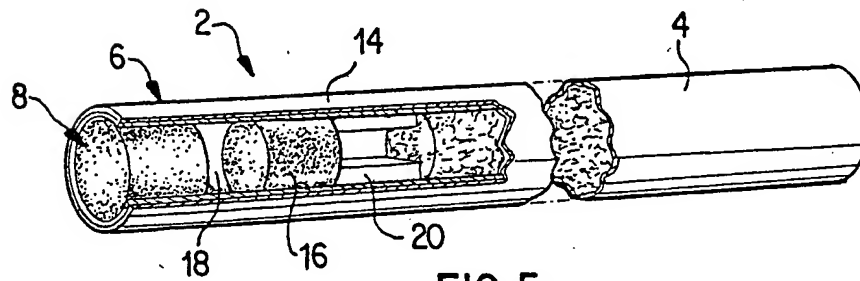


FIG. 5

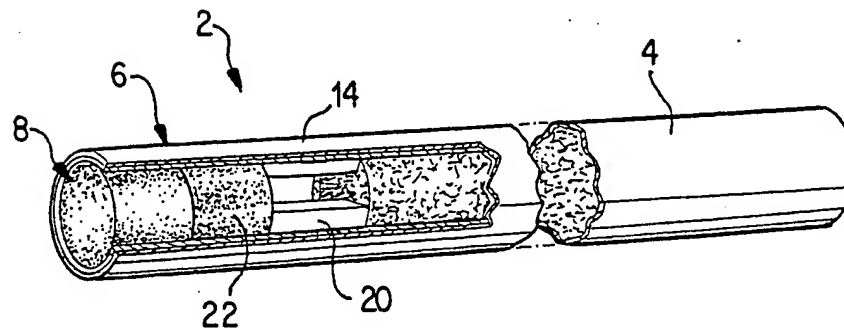


FIG. 6

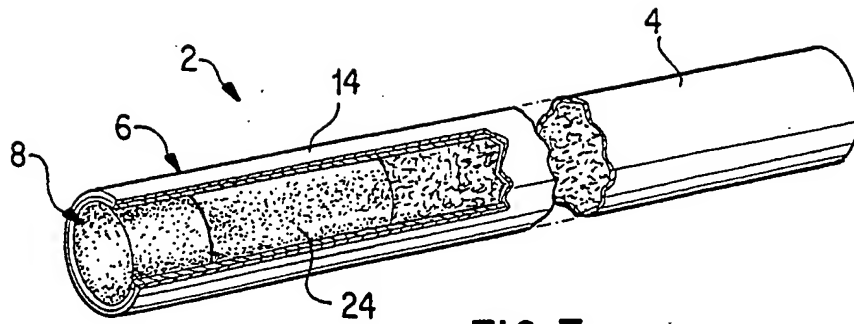


FIG. 7

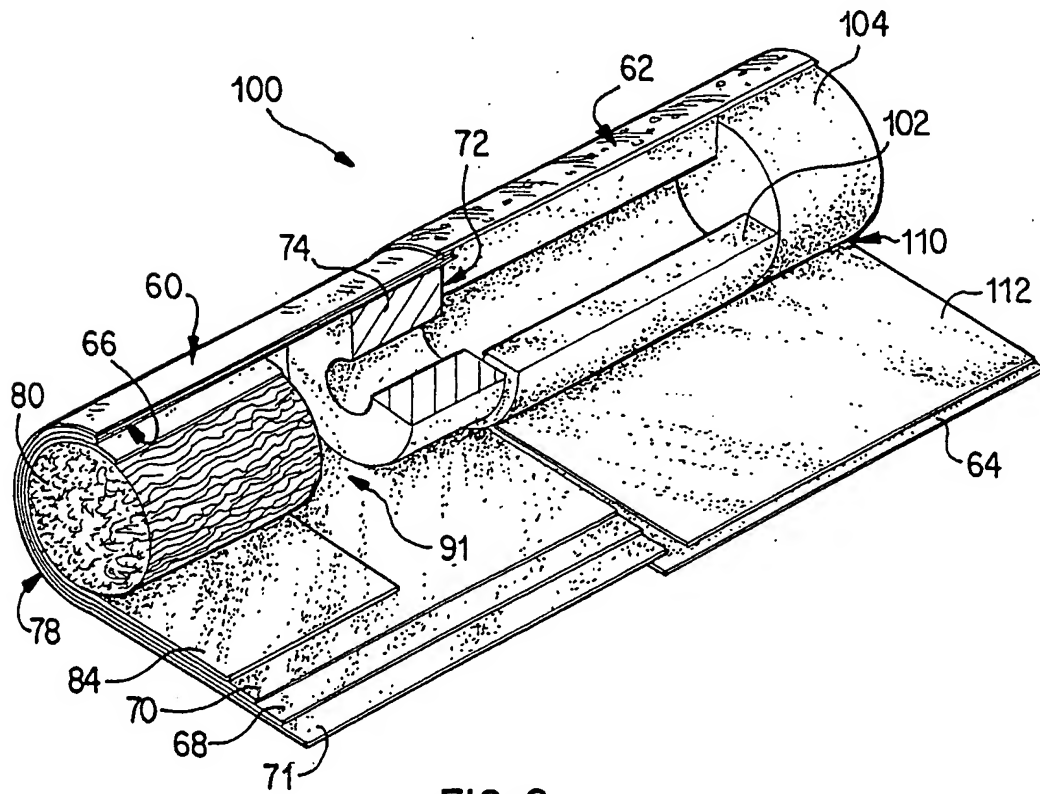


FIG. 8

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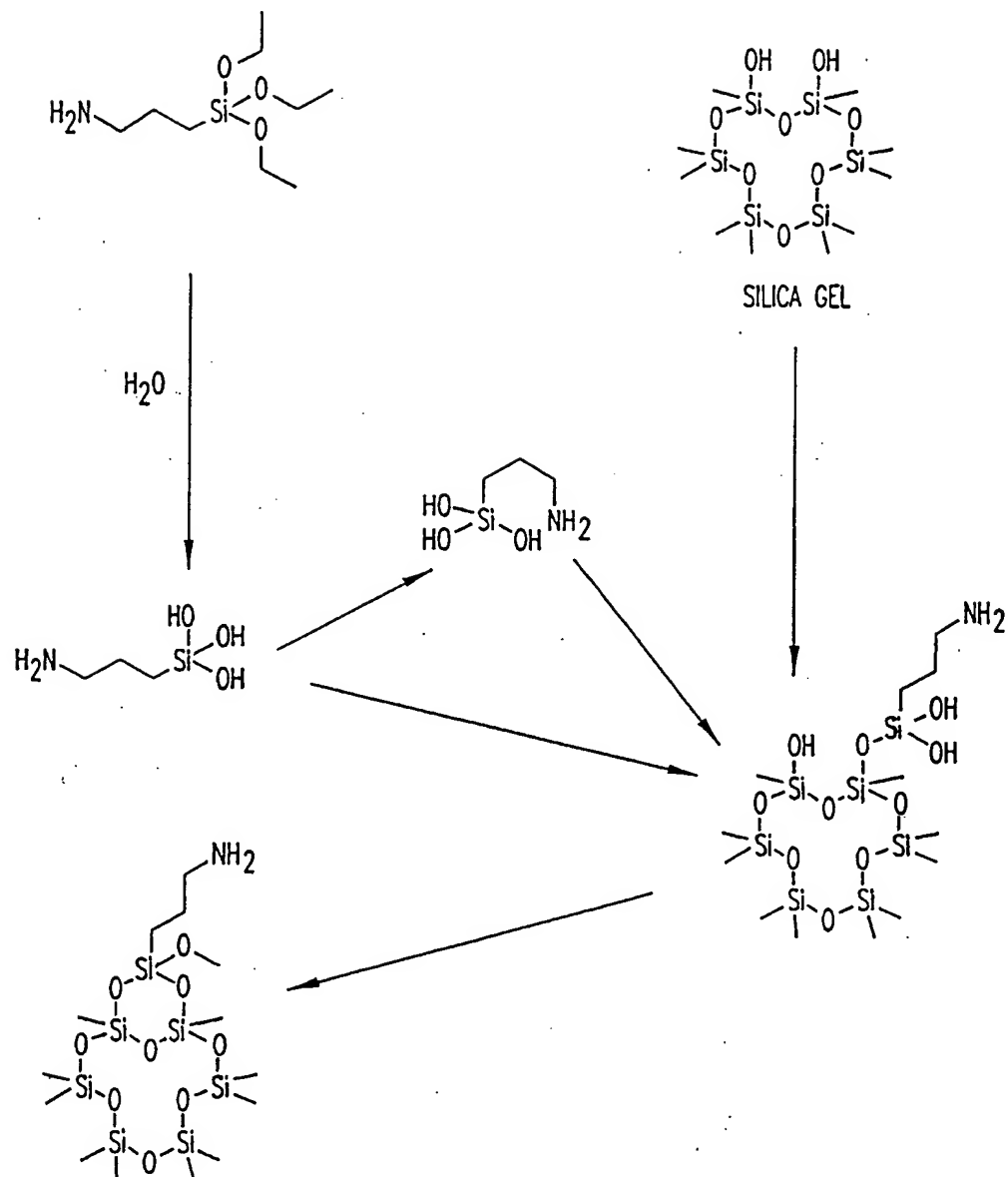


FIG.9

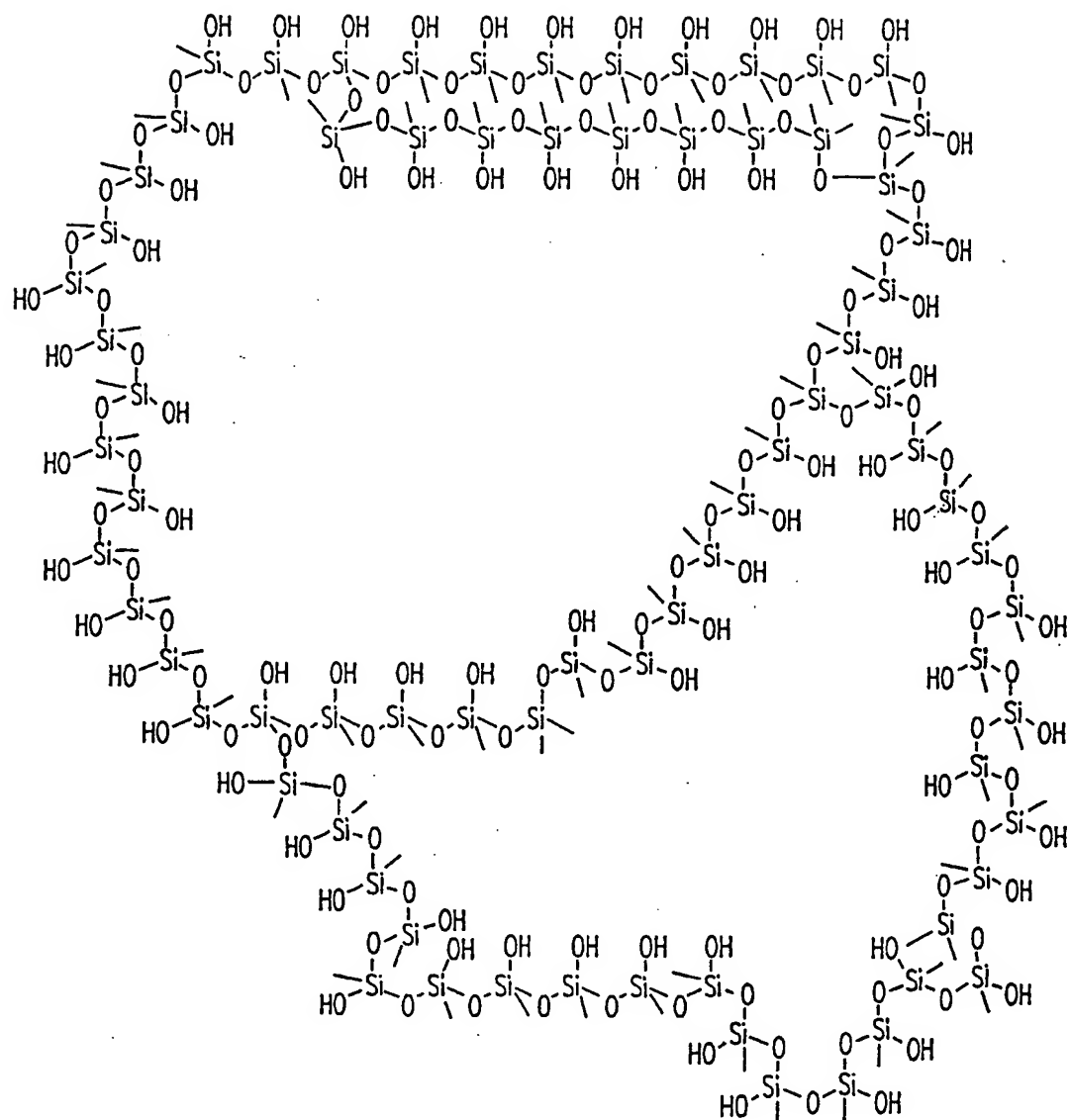


FIG.10

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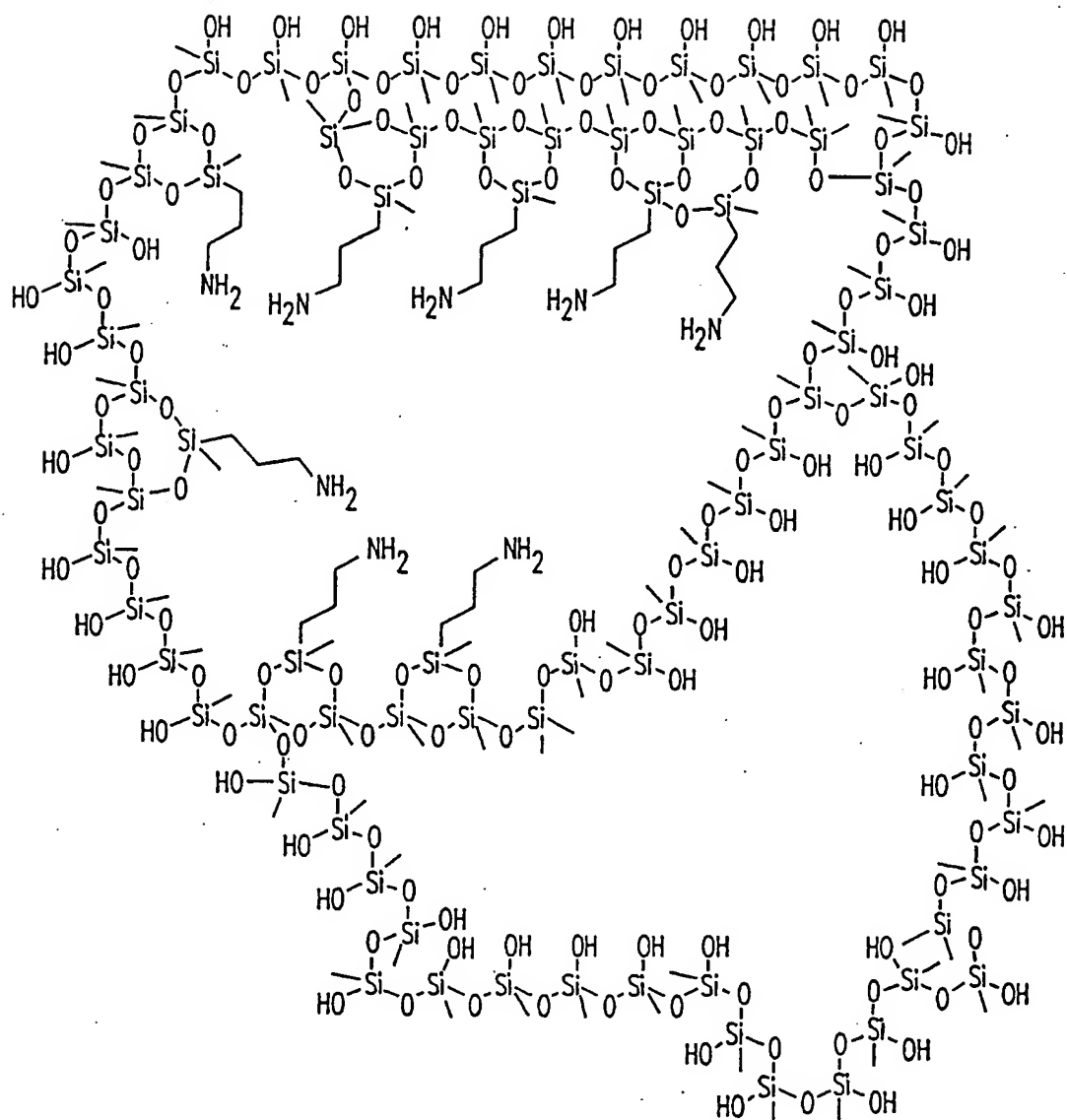


FIG. 11

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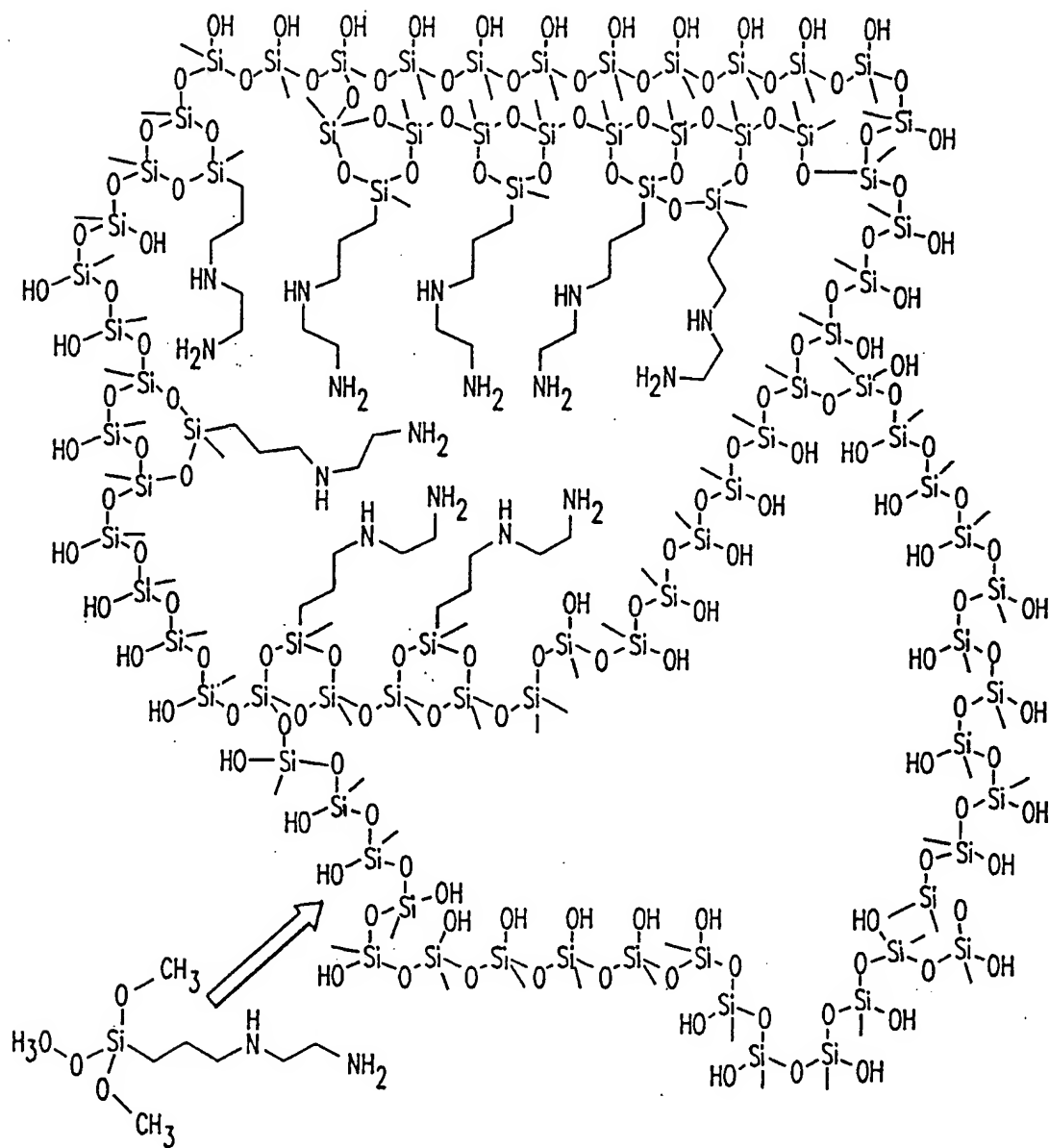


FIG. 12

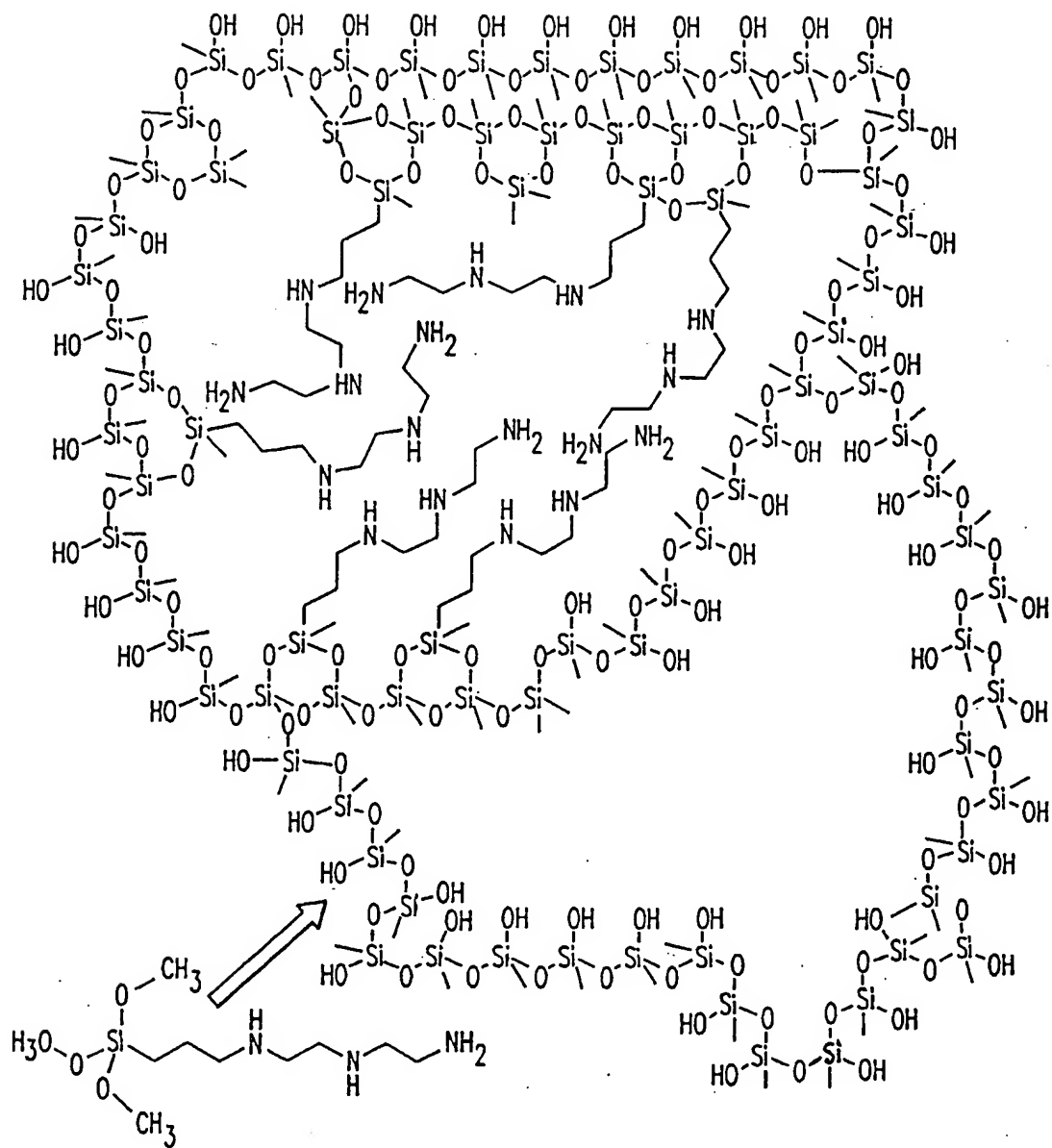


FIG. 13



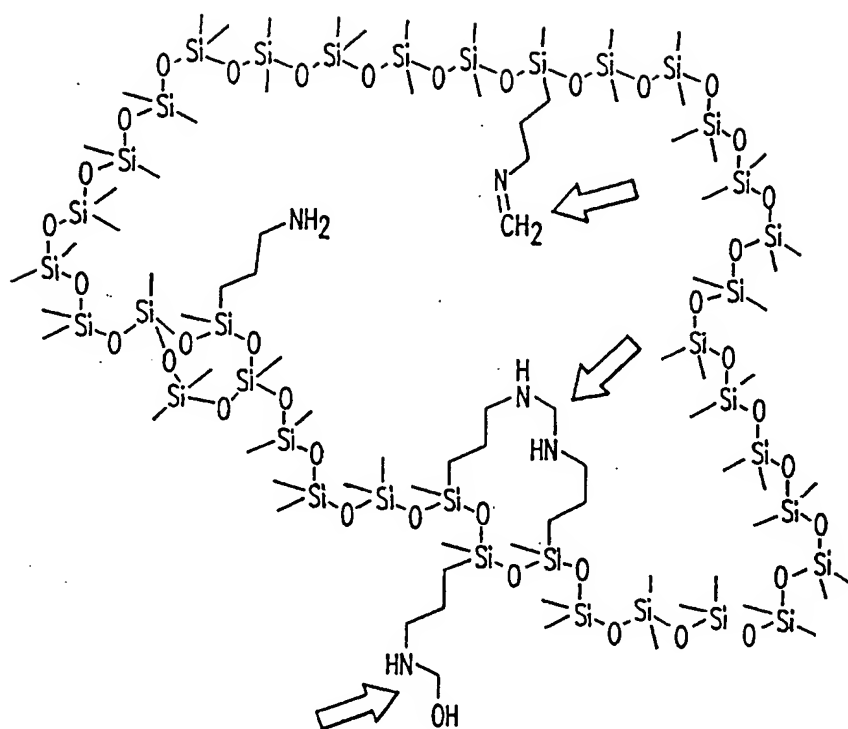


FIG. 14

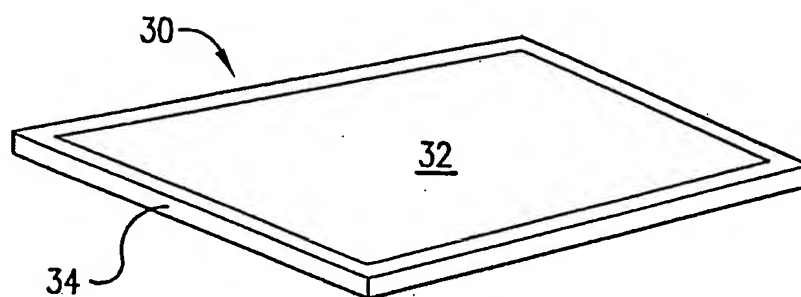


FIG. 15

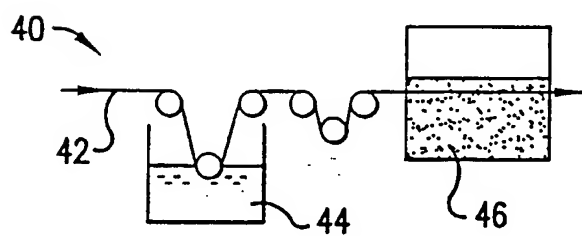


FIG. 16

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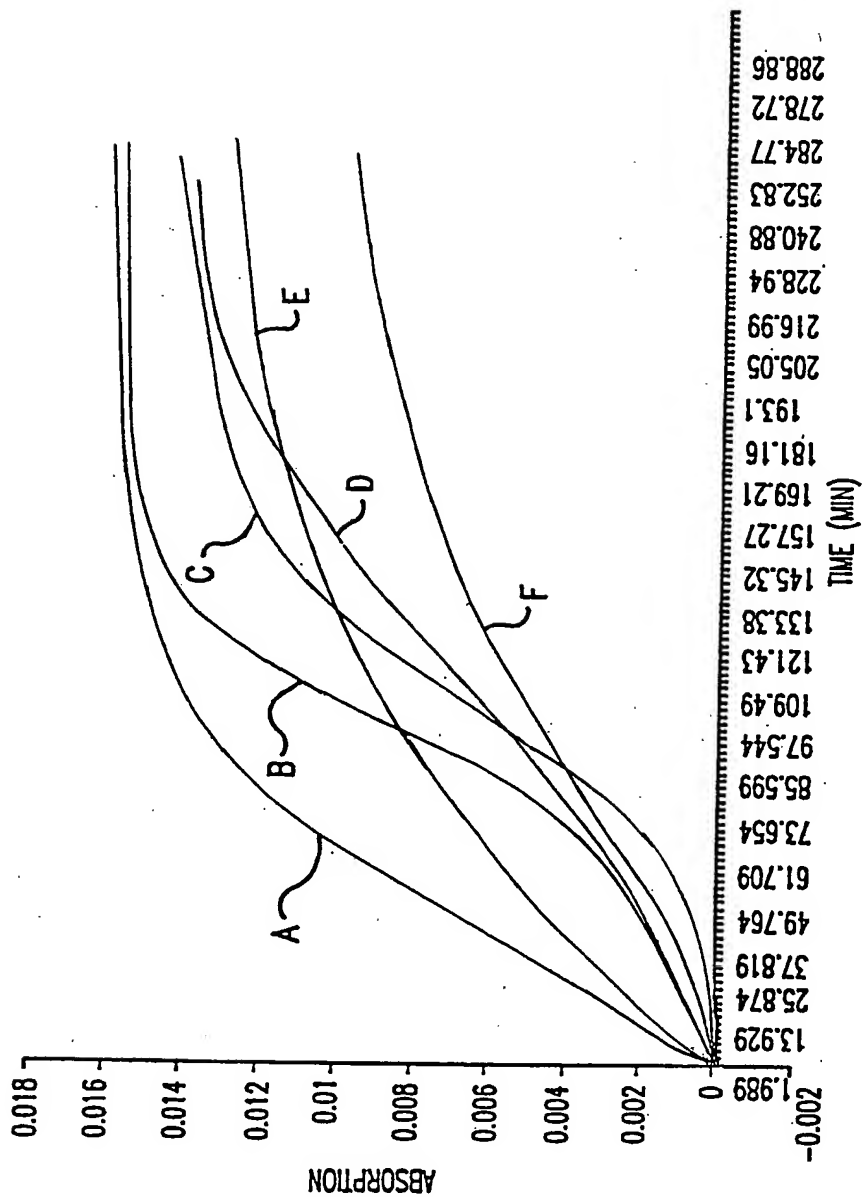


FIG. 17

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/25427

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A24B 15/28; A24B 15/18; A24B 15/00

US CL : 131/332, 334, 331, 202

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 131/332, 334, 331, 202; 423/228, 210, 245.1, 242.7

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST/WEST Electronic On-line Searching

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,892,719 A (GESSER et al) 09 January 1990, col. 1, lines 6-10; 53-68; col. 2, lines 1-4; 15-35	1-6, 8-28, 30-31, 34-37, 39-43, 45-46
Y	US 4,300,577 A (HORSEWELL et al.) 17 November 1981, col. 1, lines 24-63; col. 2, lines 12-31, see abstract.	1-8, 10-30, 32-47
Y	US 3,003,504 A (TOUEY et al.) 10 October 1961, col. 1, lines 9-11, 63-69; col. 5, lines 24-32	7, 29, 42

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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Date of the actual completion of the international search

12 DECEMBER 1999

Date of mailing of the international search report

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